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PHOTODISSOCIATION OF GASEOUS IONS FORMED BY LASER  
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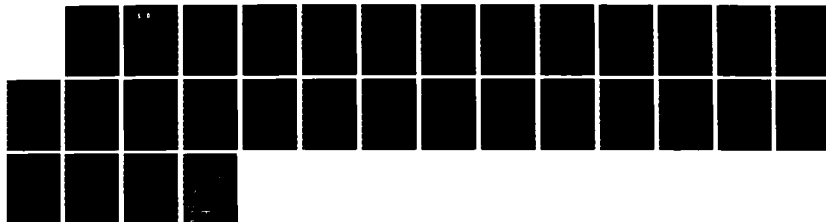
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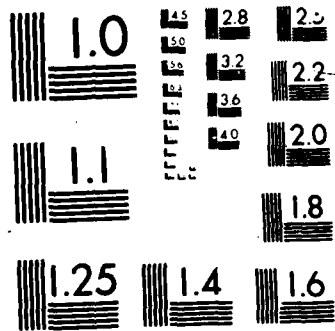
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C. H. Watson, G. Baykut and J. R. Eyler

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LASER PHOTODISSOCIATION OF GASEOUS IONS FORMED BY LASER DESORPTION

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ABSTRACT

Both pulsed and gated continuous wave carbon dioxide lasers have been employed to desorb ions and then to photodissociate them in a Fourier transform ion cyclotron resonance mass spectrometer. Pulsed CO<sub>2</sub> laser irradiation was most successful in laser desorption experiments, while a gated continuous wave laser was used for a majority of the successful infrared multiphoton dissociation studies. Fragmentation of ions with  $m/z$  values in the range 400-1300 was induced by infrared multiphoton dissociation. Such photodissociation was successfully coupled with laser desorption for a number of different classes of compounds. Either two sequential pulses from a pulsed carbon dioxide laser (one for desorption and one for dissociation) or one desorption pulse followed by gated continuous wave irradiation to bring about dissociation were utilized.



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## BRIEF

Pulsed and continuous wave carbon dioxide (infrared) lasers have been used successfully to form ions by laser desorption and to dissociate them by infrared multiphoton dissociation in a Fourier transform ion cyclotron resonance mass spectrometer.

## INTRODUCTION

The technique of laser desorption (LD) has been widely used in mass spectrometry<sup>1,2</sup> to desorb and ionize high molecular weight or other nonvolatile samples, most often using time of flight<sup>3,4</sup> or Fourier transform ion cyclotron resonance (FTICR)<sup>5,6</sup> mass spectrometers for mass analysis. A sample is inserted into the vacuum system of a mass spectrometer where it is desorbed and ionized by highly focussed laser irradiation, most often with a power density of at least  $10^8$  W/cm<sup>2</sup>.

The primary advantage of laser desorption is that abundant molecular or pseudomolecular ions are produced for many different classes of compounds. Positive pseudomolecular ions are most often formed by attachment of a cation, typically a proton, potassium or sodium ion, to the parent molecule. Negative pseudomolecular ions can also be formed by laser desorption, usually by loss of a proton. Often little fragmentation occurs and the strong molecular ion signal ( $M^+$ ,  $(M + H)^+$ ,  $(M + Na)^+$ ,  $(M + K)^+$ ,  $M^-$ , or  $(M - H)^-$ ) provides molecular weight information.

Although an abundant molecular ion peak is important in identifying the molecular weight of a compound, fragmentation is often desirable to characterize the molecular and/or ionic structure. Several techniques have been applied to achieve fragmentation; most notable are collision induced dissociation<sup>7</sup> and photodissociation.<sup>8</sup> Thus, it would be advantageous to combine one of these techniques with laser desorption to obtain both molecular weight and structural information. One possible drawback of collision induced dissociation is difficulty in dissociating larger ions<sup>9-11</sup> because of the inability to impart sufficient internal energy to them in collisions with much lighter target gases. Also, energy sufficient to dissociate a smaller ion could be "lost", that is, randomized along the many vibrational modes of a significant-

ly larger ion resulting in a lifetime before dissociation which is longer than the ion's transit time in a conventional mass spectrometer. However, irradiative pumping of moderately large molecular compounds by infrared lasers has been observed to bring about photofragmentation. In this paper the successful combination of the laser desorption and photodissociation (PD) techniques is reported.

#### EXPERIMENTAL SECTION

Experiments were carried out in a Nicolet FT/MS - 1000 mass spectrometer. The important features of this technique have been described elsewhere.<sup>12</sup> The standard laser desorption interface supplied by the manufacturer was used. As shown by the solid line in Figure 1, light from a Lumonics TE 860 grating-tuned pulsed CO<sub>2</sub> (infrared) laser (PIRL) entered the vacuum chamber through a ZnSe window and was focused by a ZnSe lens of 1.25 cm diameter and 5 cm focal length onto a solids probe containing the analyte. An Apollo 570 continuous wave grating-tuned CO<sub>2</sub> (infrared) laser (CWIRL), gated by a trigger pulse from the FTICR electronics, was also employed for laser desorption. However, its output was of insufficient power density to generate ions reliably and so its usage was limited.

Both the PIRL and CWIRL were employed for the photodissociation of gaseous ions produced by laser desorption. The CWIRL has a maximum output power of 50 watts at 10.61 micrometers and a beam diameter of 6 mm. The PIRL produces 2.6 joules in a pulse of 1 microsecond duration at 10.61 micrometers and has a 2 X 3 cm rectangular beam shape. Modifications of the FTICR which facilitate ion irradiation have been reported previously<sup>13</sup>.

In the "one laser experiment" (Fig. 1), the ions were desorbed by a single laser pulse using a focussing lens and then a mirror outside the vacuum chamber was rotated so that a second unfocussed laser pulse entered the ana-



lyzer cell and irradiated the ions. The external mirror was then returned to its original position for the next experiment. Unfortunately, a very large  $K^+$  signal was observed for both the focussed and unfocussed pulses. The potassium source is thought to be the insulating ceramic used in the FTICR cell.

Difficulty in eliminating the potassium ion formed during the second laser pulse and slight misalignment of the laser beam when moving the external mirror suggested the use of a second laser, the CWIRL, to photodissociate ions produced by the PIRL. In the "two laser" experiment the conventional solids probe was replaced by a NaCl window mounted on a hollow tube (SWT) which extended into the vacuum chamber to within a few millimeters of the FTICR cell. The analyte was dissolved in either acetone or ethanol and deposited using a micropipette on the end of the tube opposite the window and nearest the cell. This assembly served as both sample support and as a second window for laser irradiation of the ions. Following sample preparation the SWT was inserted into the vacuum chamber through the solids probe inlet. As shown in Figure 2 the PIRL beam was directed into the cell using the normal desorption optics to desorb the ions in the normal manner. The CWIRL beam entered the vacuum chamber through the salt window mounted on the SWT. Ions were formed from a focussed PIRL pulse and after a delay of 1-3 seconds to allow the initial pressure burst due to desorbed neutrals to dissipate the CWIRL irradiated the ions for 0.5-3 seconds until significant photodissociation was observed.

The SWT could be rotated and divided into 8 different areas where there was no overlap of the PIRL beam. Sample on each area produced significant ion signal for a range of 3-20 laser pulses depending on the sample and preparation characteristics. The standard experimental method employed involved collection of a LD, LD/PD, and second LD mass spectrum, giving a reference spectrum before and after the LD/PD spectrum and eliminating the possibility

of the photofragments originating from some unknown source.

Samples were obtained from commercial sources where available or submitted from various research laboratories. Sample purity was confirmed by wide mass range spectra and the samples were used without further purification.

## RESULTS AND DISCUSSION

### Laser desorption with the (gated) continuous wave laser.

Initial attempts to perform LD with the CWIRL were of limited success. Although,  $K^+$  and  $(M + K)^+$  from a sucrose sample were observed, low signal-to-noise (S/N) ratios and lack of reproducibility hindered these experiments. A 25 millisecond gated pulse from the CWIRL used for LD had a focussed power density of ca.  $2 \times 10^3$  W/cm<sup>2</sup>. This is substantially below the currently accepted lower limit<sup>14</sup> for reliable LD results. It was observed, however, that reasonably intense and reproducible ion signals could be obtained for preformed ions using the gated CWIRL. For example, both the organic cation and perchlorate anion of rhodamine-6G perchlorate were observed in positive and negative LD mass spectra, respectively.

### Laser desorption with the pulsed laser.

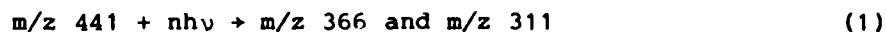
The PIRL had sufficient power to produce abundant ions and substantial molecular ion intensity has been observed in approximately 90% of samples analyzed in this laboratory to date. Excellent S/N ratios and fair reproducibility were usually obtained.

### Photodissociation of large ions.

Isomeric differentiation studies by photodissociation<sup>13</sup> and comparison of photodissociation with collision induced dissociation in FTICR<sup>15</sup> have shown the usefulness of the former in obtaining structural information about relatively small gaseous ions. The work reported here resulted from successful

attempts to extend PD methods to much larger ions. These larger ions, with their many degrees of freedom and higher density of states, are expected to appear "black" in the infrared region; that is, their infrared absorption spectrum should be nearly continuous, leading to a high probability that they will absorb infrared laser photons. The question of whether internal excitation produced by infrared absorption would be relaxed by radiative or collisional processes faster than it might accumulate in certain modes leading to bond rupture was of great interest. Initially, three different larger molecular weight samples gently heated on a solids probe and ionized by electron impact were studied. The three ions discussed below underwent photodissociation after being subjected to gated output of 0.5 to 2 s duration from the CWIRL under conditions similar to those reported<sup>13</sup> for smaller gaseous ions.

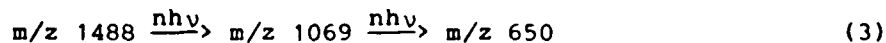
An ion of nominal  $m/z$  442 was produced from cis-dichloro-trans-dihydroxobis-2-propanamine/platinum (IV) (CHIP) by ion/molecule reactions (IMR) of the major electron impact (EI) fragment ion with the neutral molecule. As shown in Figure 3 this ion dissociated to produce two daughter photofragment ions,  $m/z$  366 and  $m/z$  311, by loss of various ligands.



Shown in Figure 4 is the photodissociation of protonated N,N'-bis(4,6-dimethylsalicylidene)-4-trifluoromethyl-o-phenylendiiminato cobalt (II) (CoSALOPH) which is also produced by ion/molecule reactions of electron impact fragments with the neutral molecule. This ion dissociated by loss of a methyl group.



The ion produced by electron attachment to tris-n-nonylfluorotriazine dissociated in a 2 step consecutive pathway as shown in Figure 5.



The above examples show that infrared multiphoton dissociation of large molecular ions can occur readily. This dissociation technique was next coupled with production of high molecular weight ions via laser desorption.

#### Use of a single laser for desorption/dissociation.

Photodissociation of small gaseous ions by a PIRL has been reported<sup>16</sup>, so an attempt was made both to form ions and to photodissociate them with sequential laser pulses from the same PIRL using the irradiation scheme shown in Fig. 1. As reported in the experimental section, a large  $K^+$  signal always appeared during the pulsed laser desorption experiment. This  $K^+$  signal was reduced somewhat by adjusting various delay times and ejecting this ion during the laser beam duration and for 50 ms following the end of the laser pulse. Time resolved LD mass spectrometry<sup>4</sup> has shown that significant amounts of  $K^+$  are formed for up to 30 milliseconds following the laser desorption pulse. Under these ejection conditions, photodissociation of the t-butylpyridinium (TBP) cation (from the perchlorate salt) produced by laser desorption was observed. As shown in Figure 6 the TBP cation,  $m/z$  138, dissociates under laser irradiation with loss of  $C_4H_8$  to produce an ion of  $m/z$  80, which is most likely protonated pyridine.



#### Use of two lasers for desorption/dissociation.

N,N'-bis(4,6-dimethylsalicylidene)-4-trifluoromethyl-o-phenylendiiminato cobalt (II) (CoSALOPH): This compound was selected as a test case since its PD pathways were known (see equation 2 and Figure 4) and significant amounts of  $(M + H)^+$  were observed following laser desorption. Photodissociation behavior observed following laser desorption was identical to that seen when electron impact was used to produce the ions (equation 2 and Figure 4).

Sucrose: Observation of the molecular ion produced by LD<sup>14</sup> and LD

followed by EI<sup>17</sup> has been reported for sucrose. The negative ion mass spectrum following laser desorption reveals a  $(M - 1)^-$  ion at  $m/z$  341. When irradiated this ion dissociates with production of ions at  $m/z$  251, 249, 179 and 161 as shown in Figure 7. The ion at  $m/z$  161 corresponds to the loss of a water molecule from one monosaccharide unit. The ion at  $m/z$  179 most likely results from loss of one monosaccharide unit. Since both glucose and fructose have identical empirical formulae it is not possible at this time to assign one or the other identity to this ion.

The two fragment ions discussed above ( $m/z$  179 and  $m/z$  161) were observed in the negative LD/EI mass spectrum<sup>17</sup> of sucrose. The fragment ions with  $m/z$  251 and  $m/z$  249, however, are unique photodissociation products. The ions formed at  $m/z$  251 and 249 correspond to loss of  $C_3H_7O_3$ , and  $C_3H_9O_3$  respectively, suggesting that one of the monosaccharide chains may have opened as a result of ionization; otherwise photodissociation brings about the cleavage of two bonds. It is not known at this time whether these ions are produced by separate pathways from the  $(M-1)^-$  ion or from consecutive photodissociations.

Hesperidin: In the negative ion LD mass spectrum of this compound an ion of  $m/z$  612 was produced from the sodium salt of hesperidin phosphoric acid ester. This ion was observed to dissociate by loss of the attached sugar to produce an ion at  $m/z$  301 when irradiated by the CWIRL as shown in Figure 8.



N-2-(5,5-diphenyl-2,4-imidazolidinedionyl-3-ethyl)-7-acetoxy-1-naphthyl sulfonamide: This substituted sulfonamide has a molecular weight of 543 amu and in the positive LD mass spectrum two ions at  $m/z$  566 and  $m/z$  582, corresponding to attachment of potassium and sodium ions, respectively, were observed. No significant PD was seen for either of these two ions. In the negative ion LD mass spectrum an ion at  $m/z$  500 originating from loss of  $C_2H_3O$

was observed. This ion photodissociated when irradiated by the CWIRL to produce an ion at  $m/z$  251 (see Figure 9).



High resolution mass analysis of the ion at  $m/z$  251 indicated that it has the empirical formula  $C_{15}H_{11}N_2O_2^-$ , and is thus the 5,5-diphenyl-2,4-imidazolidinedion anion, resulting from cleavage of C-N bond next to the imidazole ring.

#### CONCLUSIONS

The feasibility of using laser photodissociation to further fragment ions produced by laser desorption has been demonstrated for moderate molecular weight compounds. This technique should work equally well for both positive and negative ions formed by laser desorption. However, for the compounds reported here negative ion laser desorption usually produced much higher intensities of molecular or pseudo-molecular ions than the corresponding positive ion mode. Applications of ultraviolet<sup>11</sup> and two photon visible<sup>18</sup> PD have been demonstrated and could be adapted for the photodissociation of laser desorbed ions. We are extending this work to larger molecular weight compounds and will also attempt to induce further fragmentation through the use of a Nd:YAG pumped dye laser system.

#### ACKNOWLEDGMENTS

We thank Mr. Andy Griffis and Professor Russell Drago for preparation of the CoSALOPH sample, Dr. Robert Weller and Dr. Christopher Riley for donation of the CHIP sample, and Professor Alan Katritzky for the TBP perchlorate sample.

## CREDIT

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## LITERATURE CITED

1. Conzemius, R. J.; Capellen, R. J. *Int. J. Mass Spectrom. Ion Phys.* 1980, 34, 197.
2. Hillenkamp, F.; in Benninghoven, A. (Ed.) "Ion Formation from Organic Solids", Springer Verlag, Berlin, 1983.
3. Tabet, J.-C.; Cotter, R. J. *Int. J. Mass Spectrom. Ion Phys.* 1983, 54, 151.
4. Van Breemen, R. B.; Snow, M.; Cotter, R. J. *Int. J. Mass Spectrom. Ion Phys.* 1983, 49, 35.
5. McCreery, D. A.; Ledford, E. B., Jr.; Gross, M. L. *Anal. Chem.* 1982, 54, 1435.
6. Wilkins, C. L.; Weil, D. A.; Yang, C. L. C.; Ijames, C. F. *Anal. Chem.* 1985, 47, 520.
7. Levsen, K.; Schwarz, H. *Mass Spectrom. Rev.* 1983, 125, 1.
8. Thorne, L. R.; Beauchamp, J. L.; in Bowers, M. T. (Ed.) "Gas Phase Ion Chemistry", Vol. 3, Academic Press, New York, 1984, 41.
9. Amster, I. J.; Baldwin, M. A.; Cheng, M. T.; Procter, C. J.; McLafferty, F. W. *J. Am. Chem. Soc.* 1983, 105, 1654..
10. Sheil, M. M.; Derrick, P. J. *Org. Mass Spectrom.* 1985, 20, 430.
11. Bowers, W. D.; Delbert, S.-S.; McIver, R. T. *Anal. Chem.* 1986, 54, 969.
12. Comisarow, M. B. *Anal. Chim. Acta* 1985, 178, 1.
13. Baykut, G.; Watson, C. H.; Weller, R. R.; Eyler, J. R. *J. Am. Chem. Soc.* 1985, 107, 8036.
14. Van Der Peyl, G. J. Q.; Haverkamp, J.; Kistemaker, *Int. J. Mass Spectrom. Ion Phys.* 1982, 42, 125.
15. Watson, C. H.; Baykut, G.; Battiste, M. A.; Eyler, J. R. *Anal. Chim. Acta*



1985, 178, 125.

16. Jasinski, J. M.; Rosenfeld, R. N.; Meyer, F. K., Brauman, J. I. J. Am. Chem. Soc. 1982, 104, 652.

17. Hein, R. E.; Cody, R. B., Nicolet Instrument Corp., (private communication).

18. Dunbar, R. C.; Ferrara, J. J. Chem. Phys. 1985, 83, 6229.

## FIGURE CAPTIONS

Figure 1. Configuration used for single laser experiments with a pulsed CO<sub>2</sub> laser. During the first laser pulse the beam was focussed through the lens and formed ions by laser desorption. A rotatable mirror directed the second, unfocussed laser beam into the cell to fragment trapped ions by multiphoton dissociation.

Figure 2. Configuration used for double laser experiment. A pulsed CO<sub>2</sub> laser (laser 1) was used to desorb and ionize the sample and a CW CO<sub>2</sub> laser (laser 2) was used to dissociate the trapped ions.

Figure 3. Top. Ion/molecule reaction product formed by reaction of cis-dichloro-trans-dihydroxo-bis-2-propanamine platinum (IV) with its 50 eV electron impact fragments. Bottom. Fragmentation pattern produced upon irradiation with CW CO<sub>2</sub> laser, same experimental conditions and delay times as in the top spectrum.

Figure 4. Top. Protonated N,N'-bis(4,6-dimethylsalicylidene)-4-trifluoromethyl-o-phenylenediiminato cobalt (II) (CoSALOPH) formed by reaction of the neutral molecule with fragment ions produced by electron impact at 50 eV. Bottom. Fragmentation obtained upon irradiation with the CW CO<sub>2</sub> laser, same experimental conditions and delay times as in the top spectrum.

Figure 5. Top. Negative molecular ion of tris-n-nonyl fluorotriazine formed by capture of ca. 0 eV electrons. Bottom. Fragmentation obtained

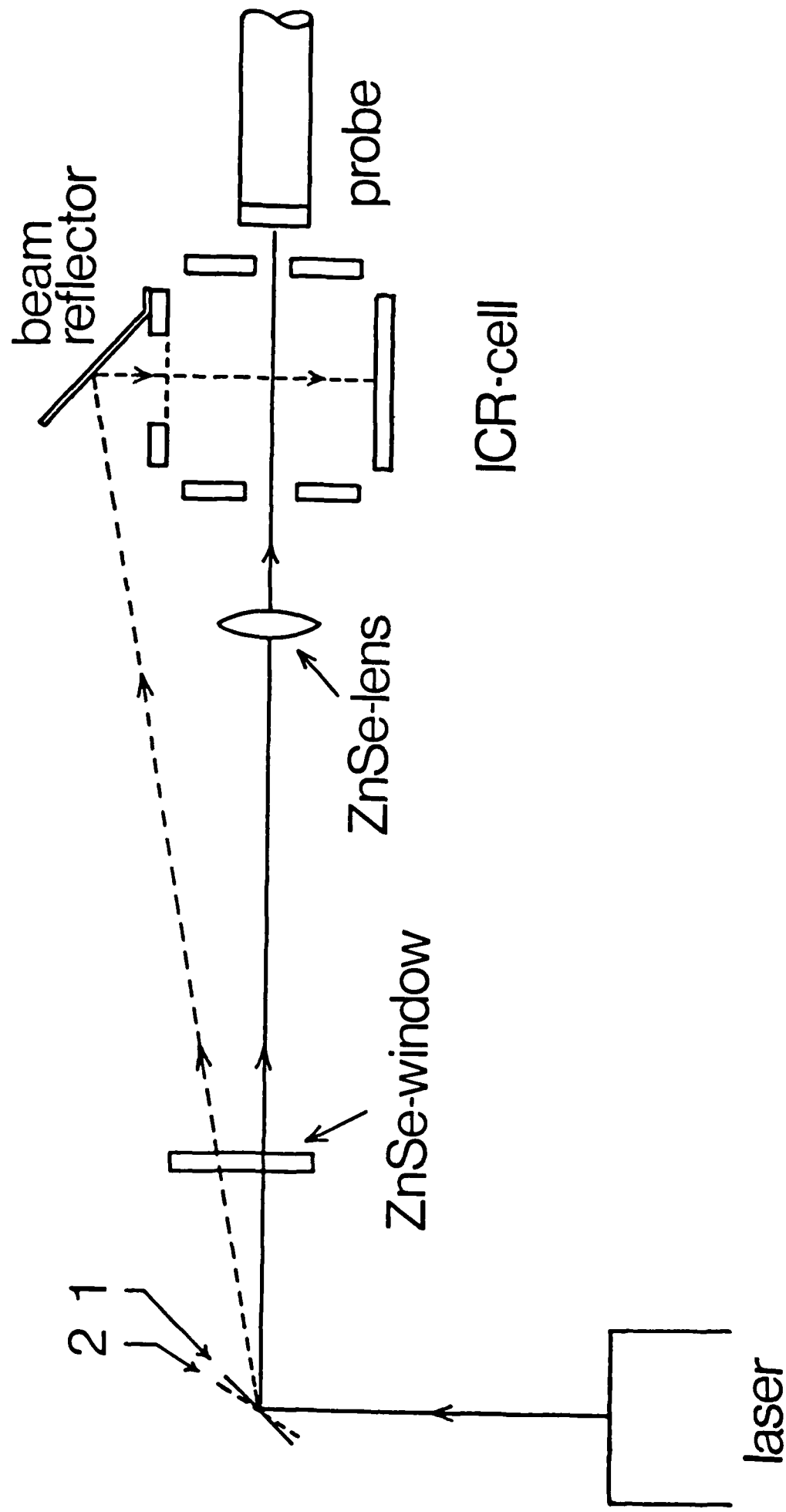
upon irradiation with CW  $\text{CO}_2$  laser, same experimental conditions and delay times as in the top spectrum.

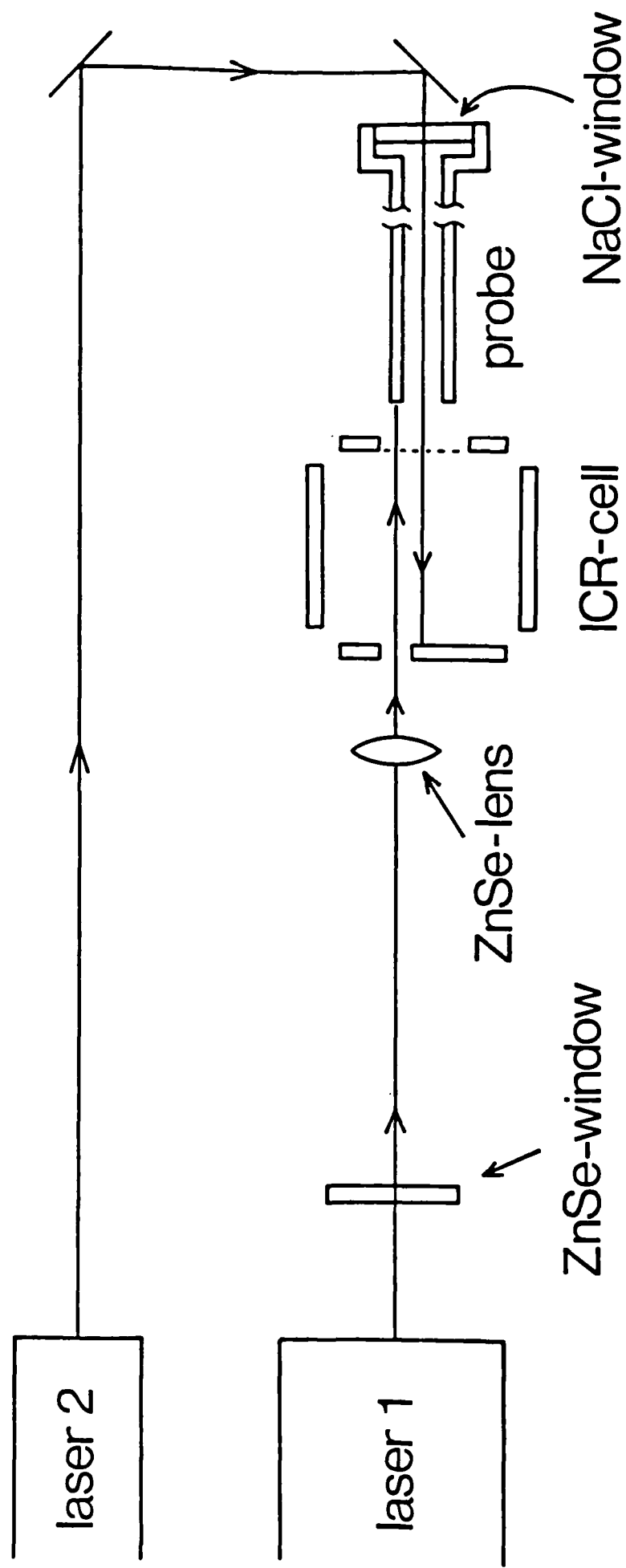
Figure 6. Top. Tert-butylpyridinium cation formed by laser desorption from its perchlorate salt. Bottom. Fragmentation achieved with a single laser pulse from a pulsed  $\text{CO}_2$  laser, all other conditions identical to the top spectrum.

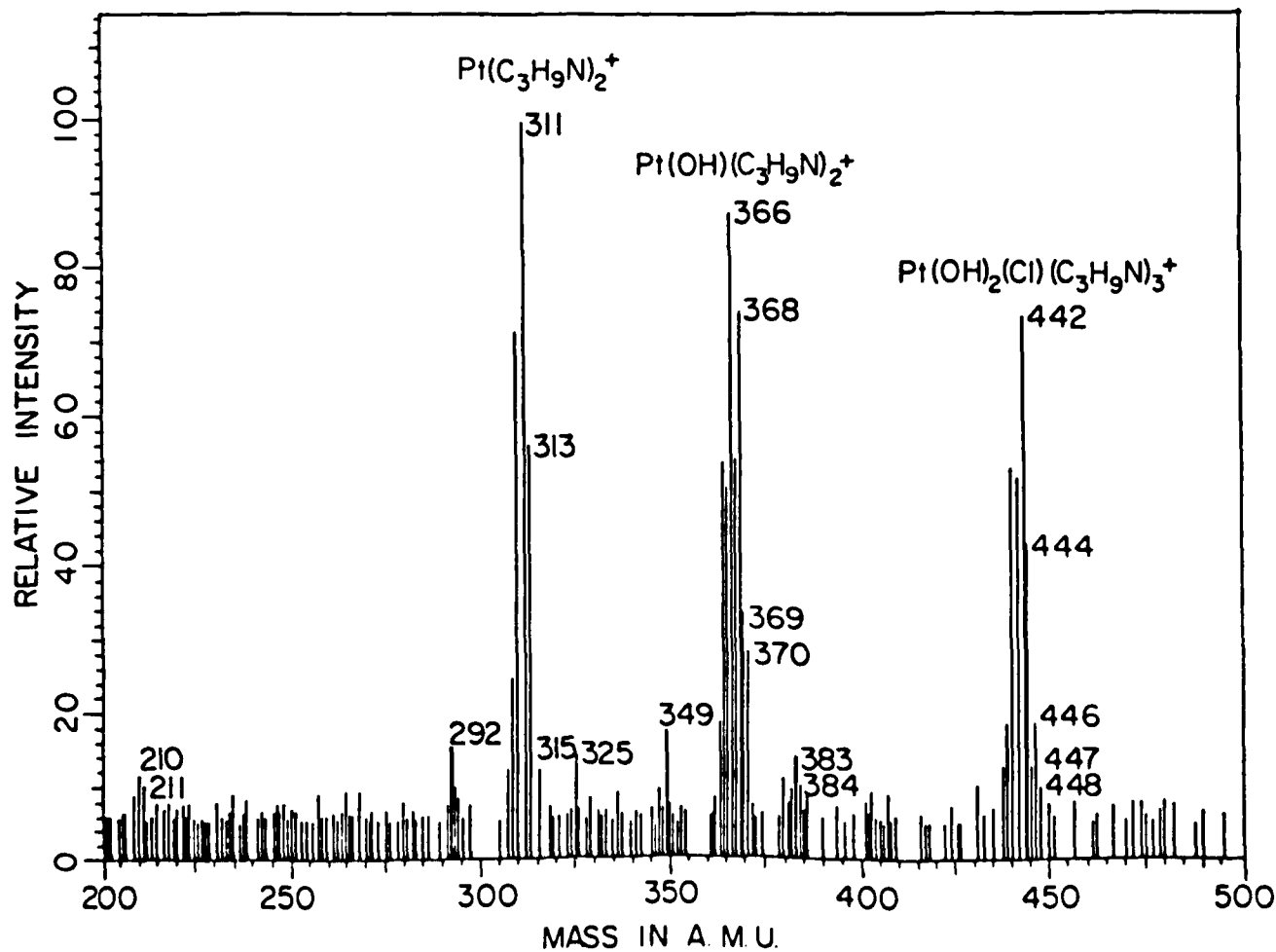
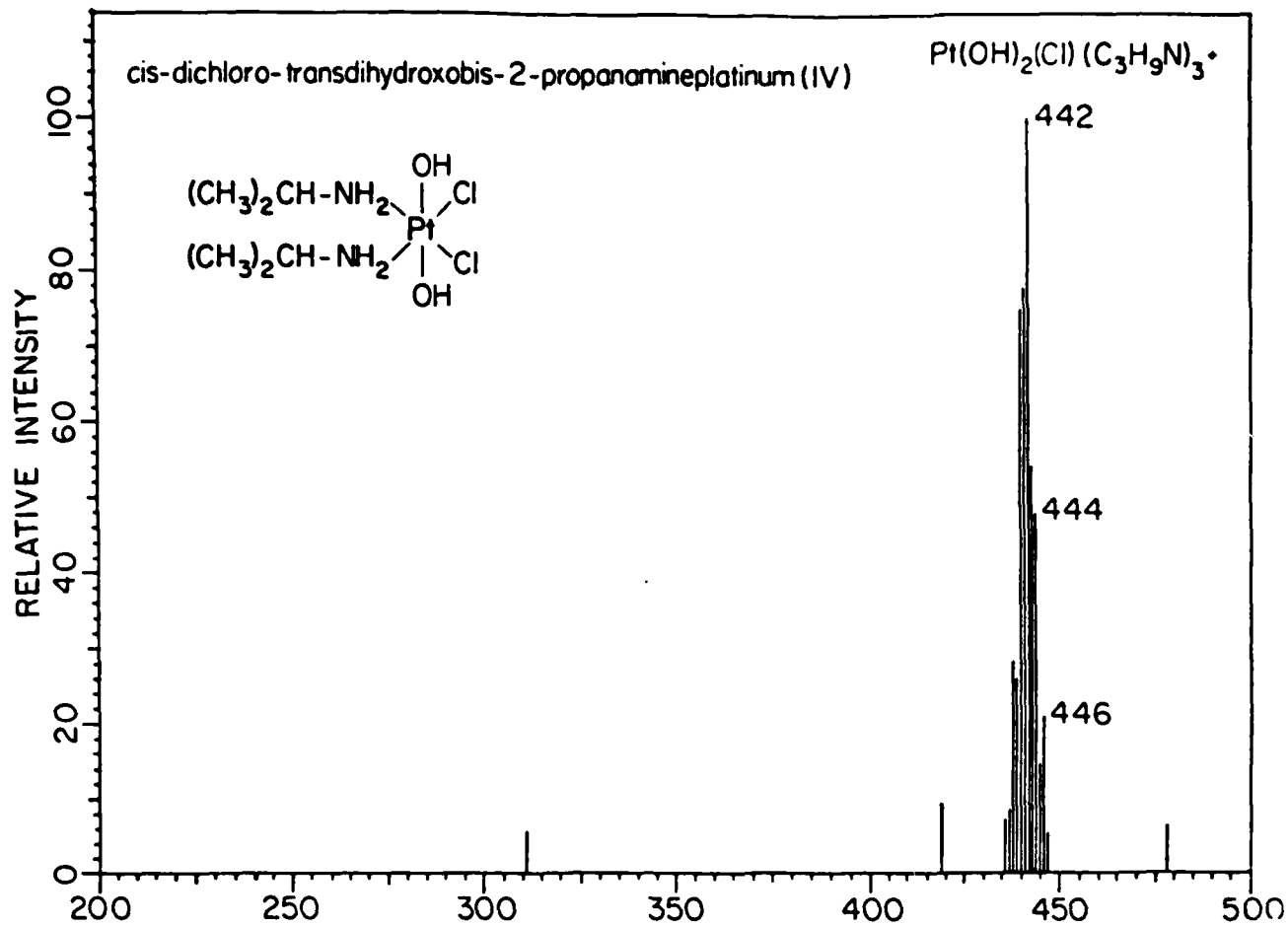
Figure 7. Top.  $(\text{M-H})^-$  ion of sucrose formed by desorption with pulsed  $\text{CO}_2$  laser beam. Bottom. Fragmentation upon irradiation with the CW  $\text{CO}_2$  laser. Experimental conditions are same as in the top spectrum.

Figure 8. Top. Negative ions formed by laser desorption from Na-salt of hesperidin phosphoric acid ester using pulsed  $\text{CO}_2$  laser. Bottom. Fragmentation upon irradiation with a CW  $\text{CO}_2$  laser. Experimental conditions are identical to those of the top spectrum.

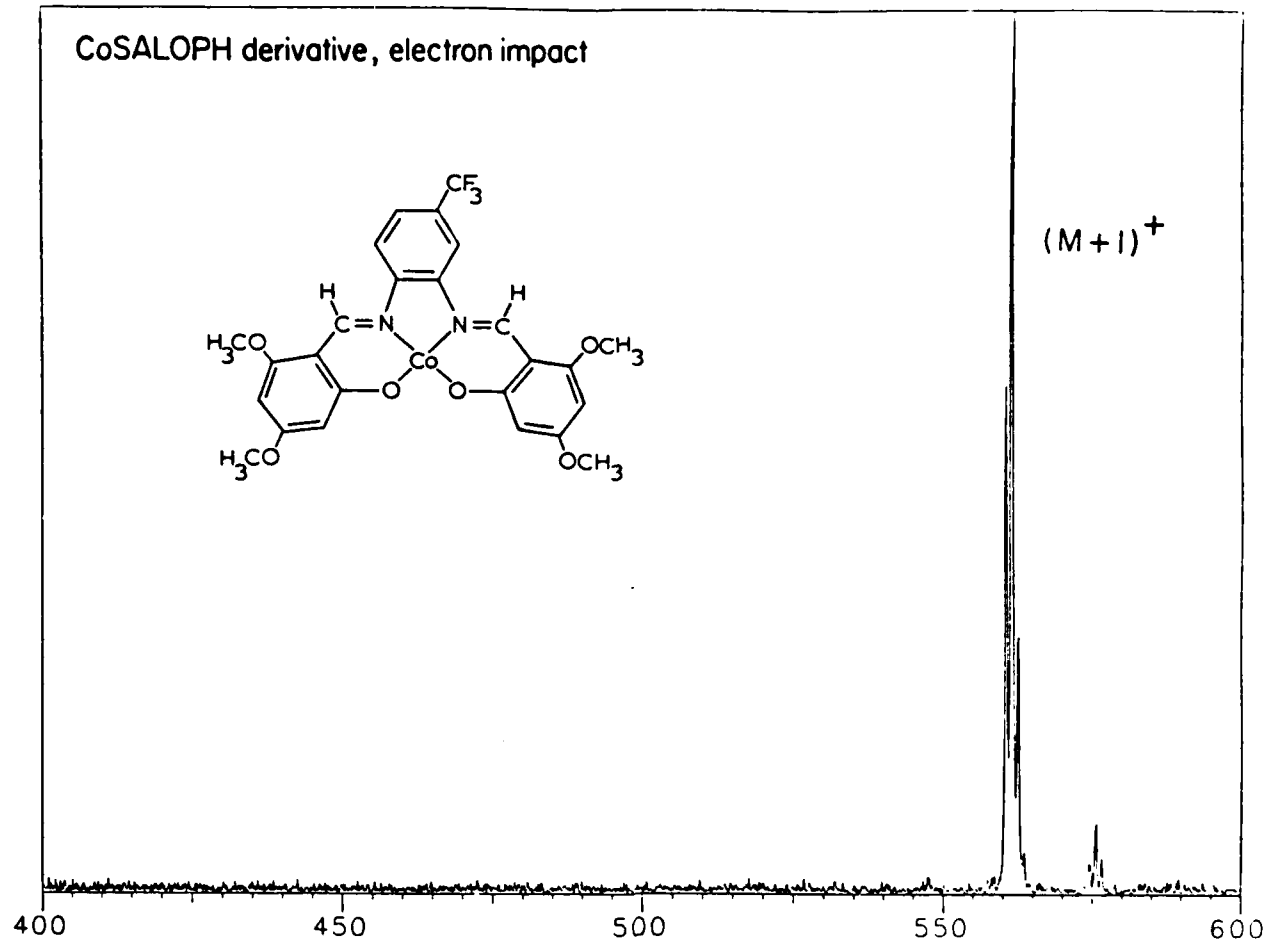
Figure 9. Top. Negative fragment ion formed from the substituted sulfonamide by laser desorption using pulsed  $\text{CO}_2$  laser. Bottom. Fragmentation upon irradiation with a CW  $\text{CO}_2$  laser, all other conditions identical to those in the top spectrum.



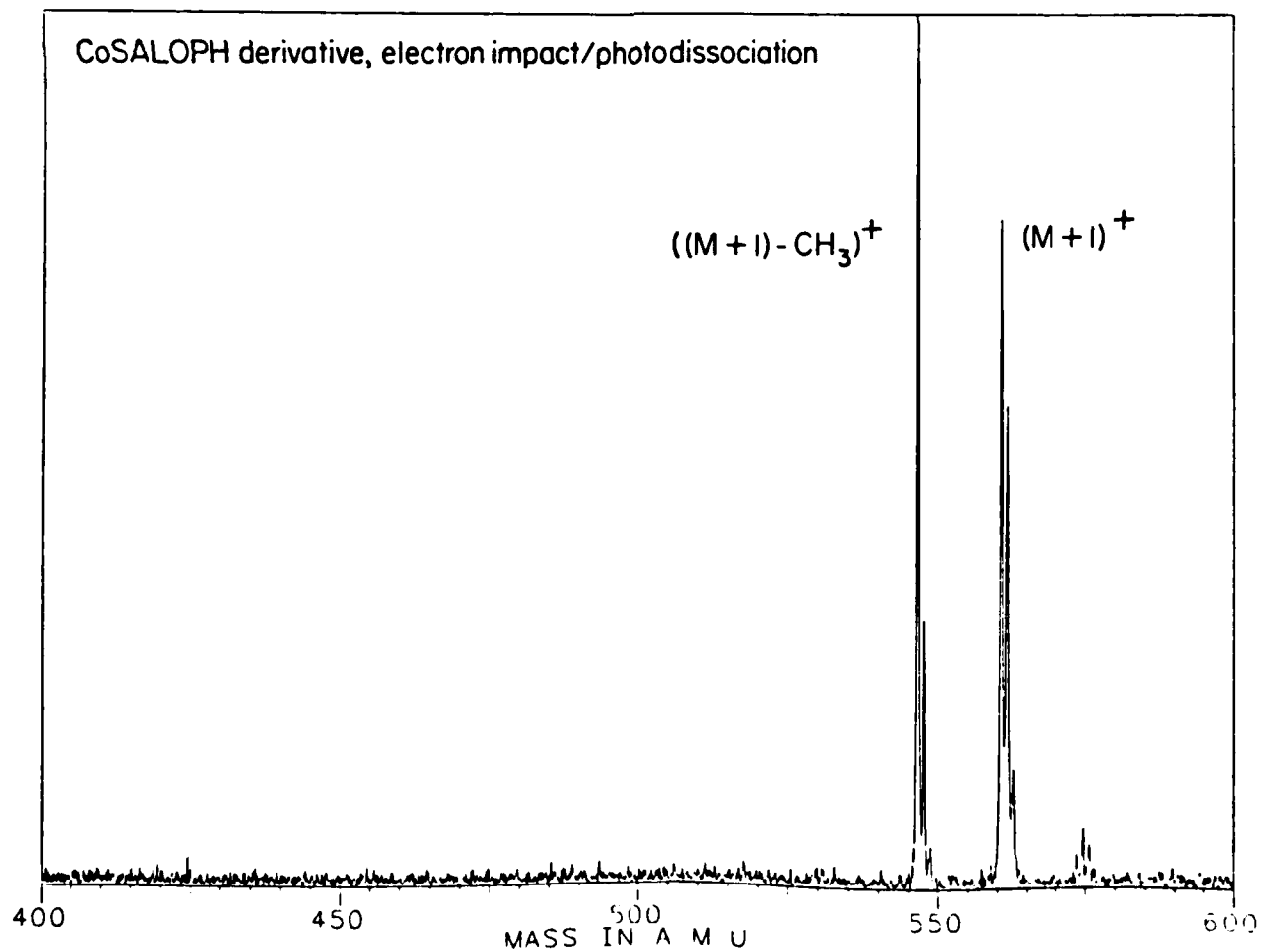




CoSALOPH derivative, electron impact

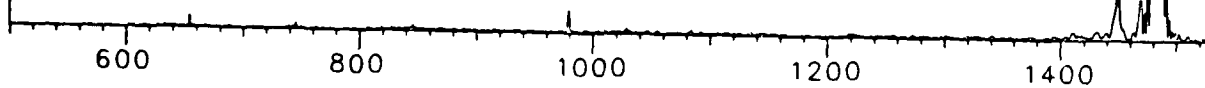
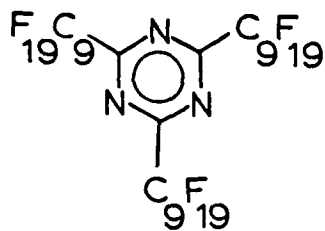


CoSALOPH derivative, electron impact/photodissociation



Tris(perfluorononyl)-s-triazine,  
electron impact, negative ions

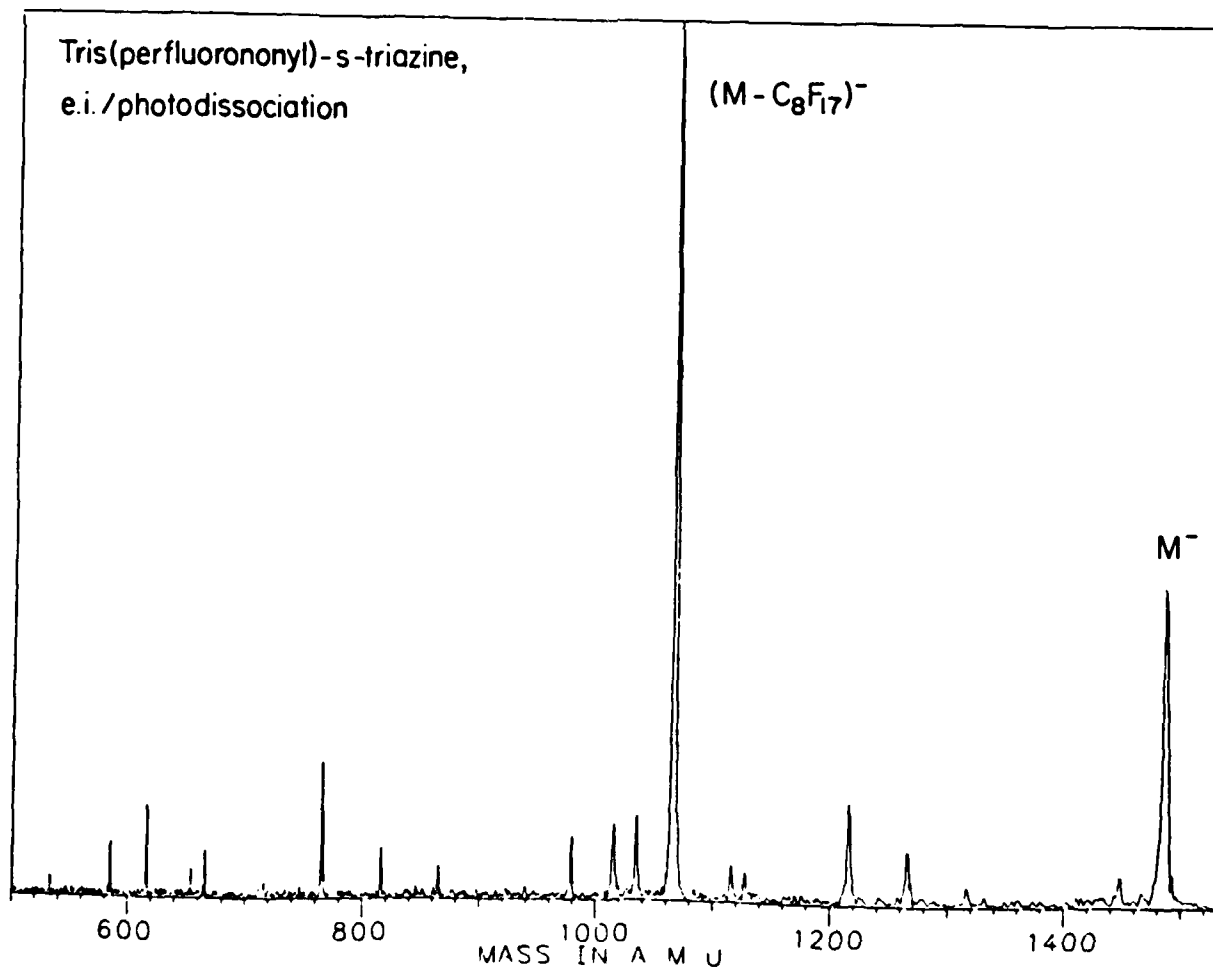
$M^-$



Tris(perfluorononyl)-s-triazine,  
e.i./photodissociation

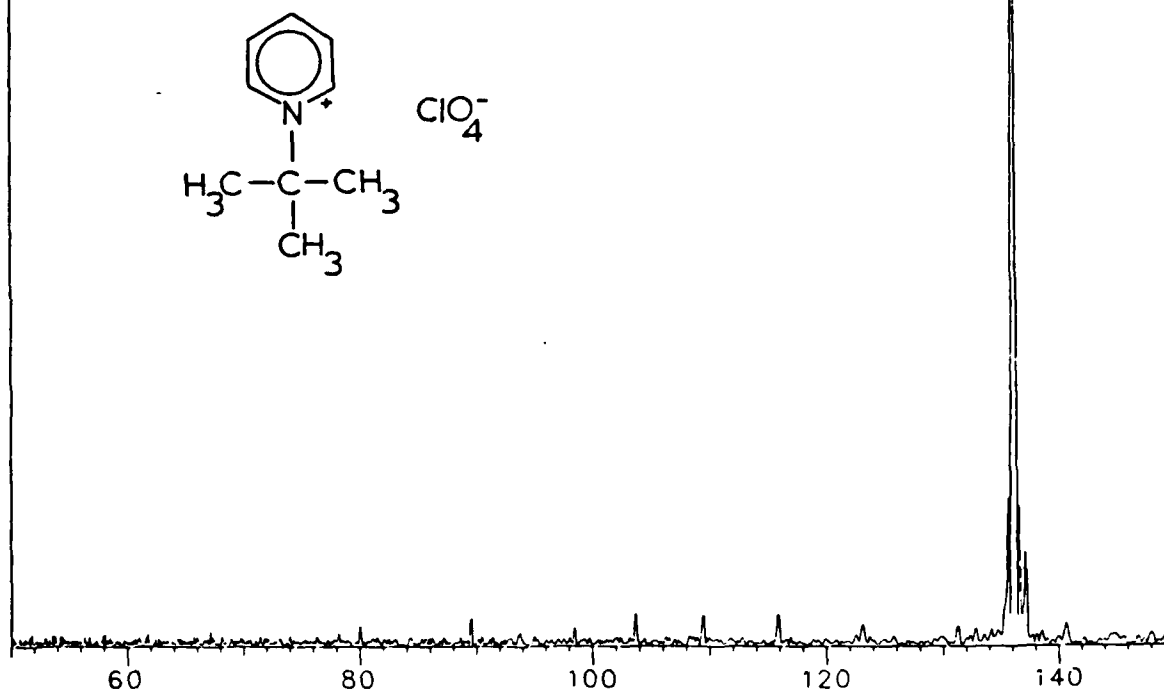
$(M - C_8F_{17})^-$

$M^-$

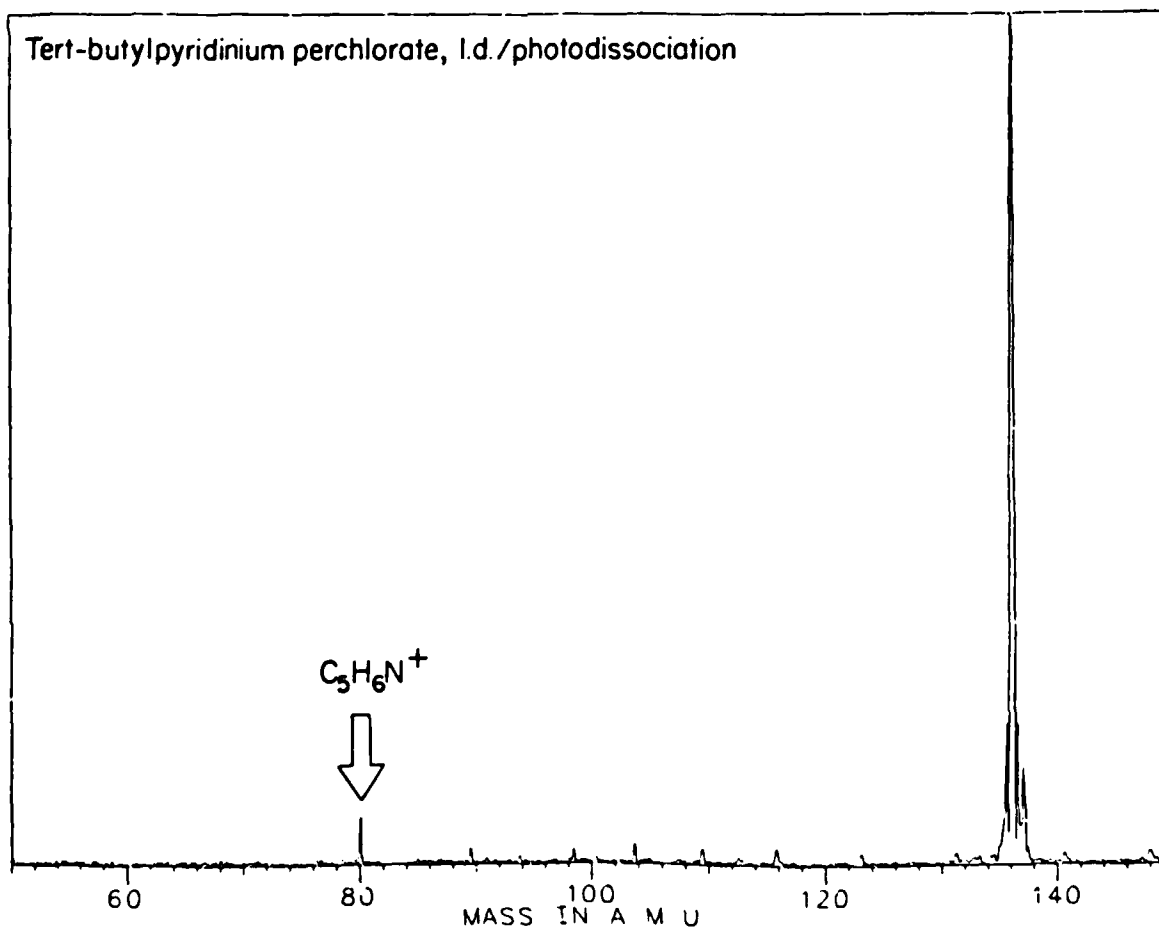




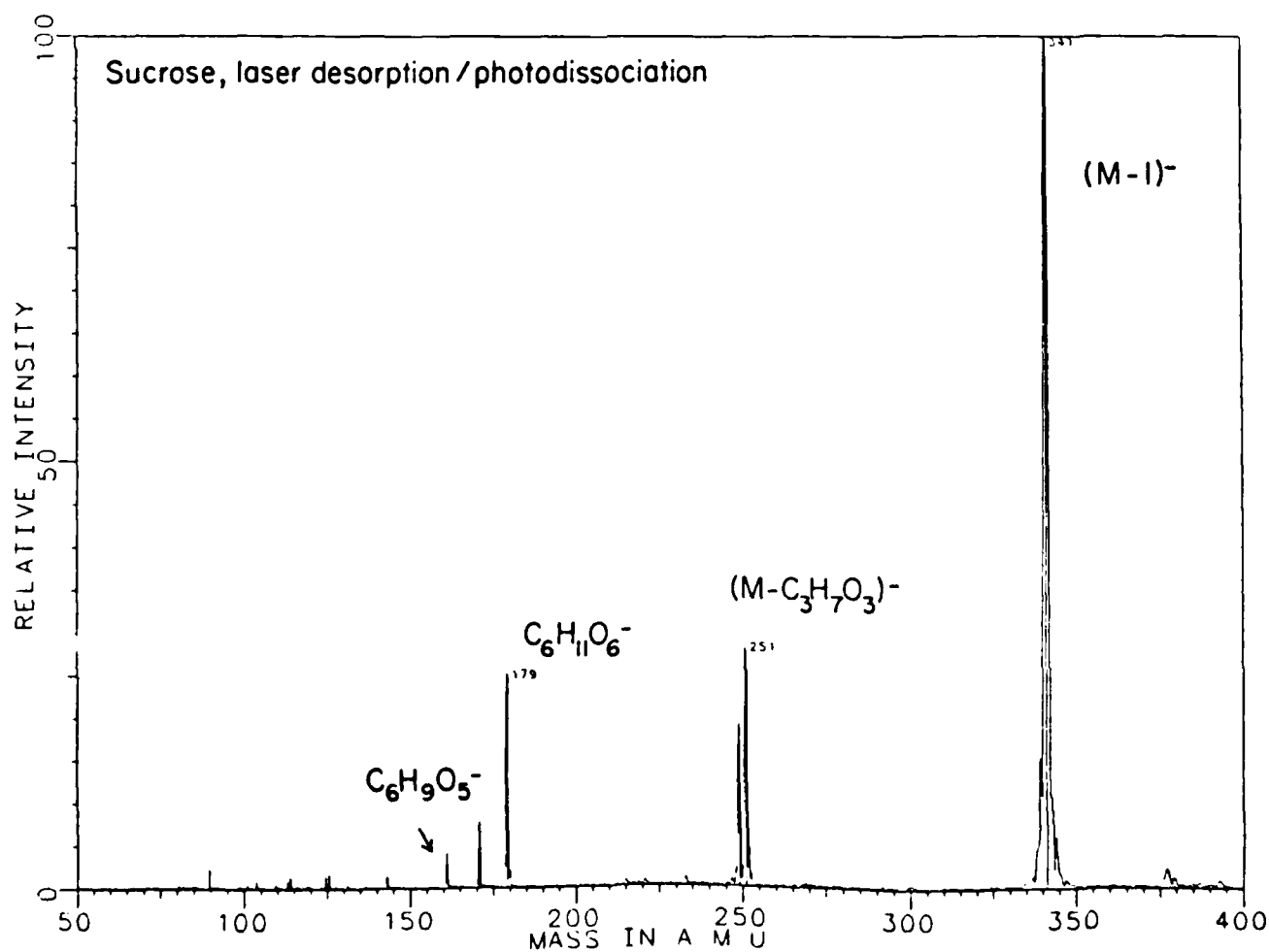
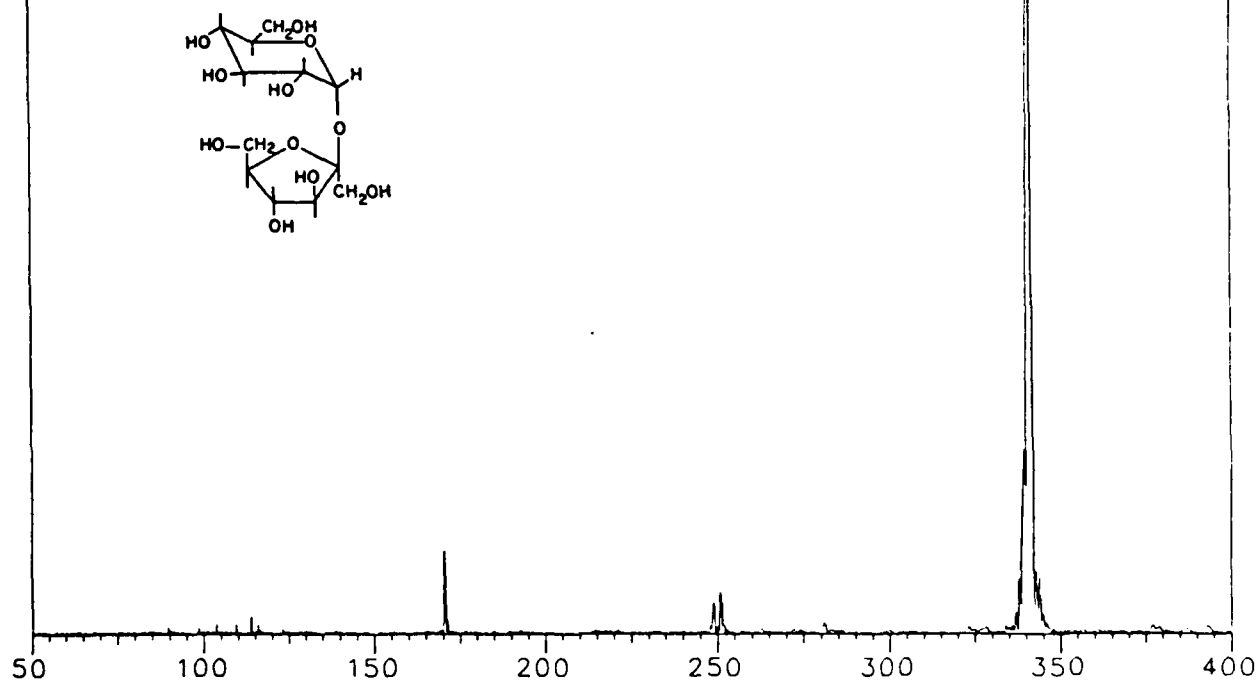
Tert-butylpyridinium perchlorate, laser desorption



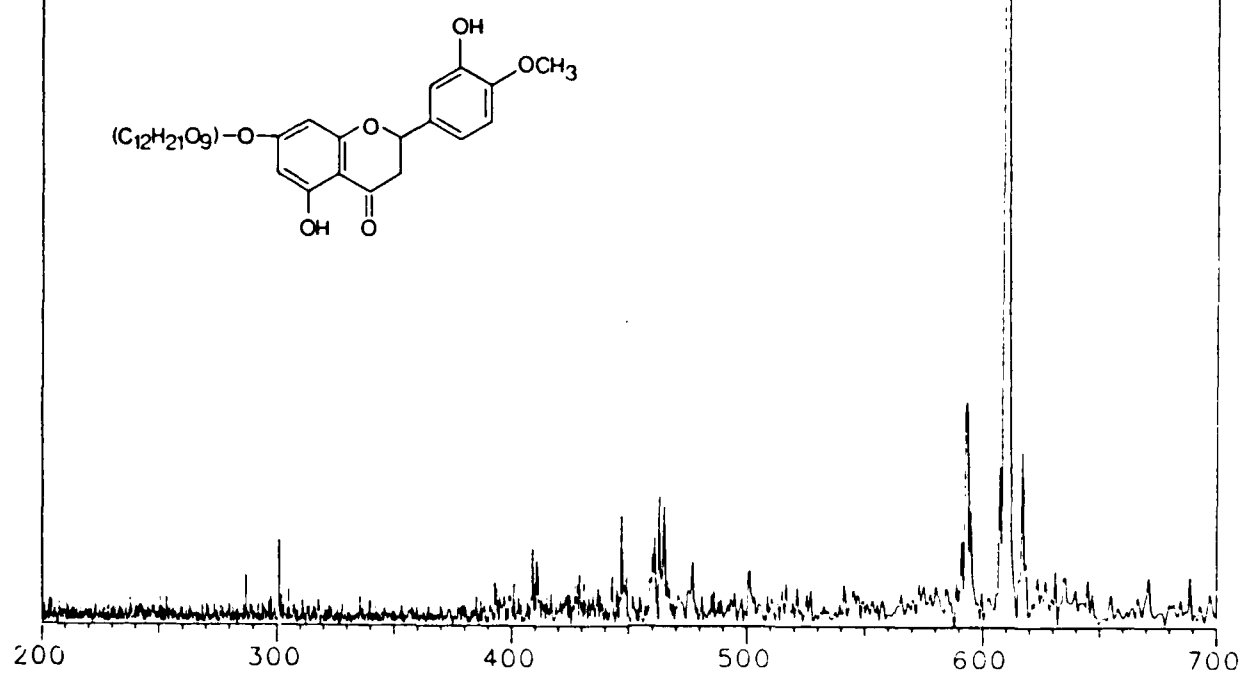
Tert-butylpyridinium perchlorate, I.d./photodissociation



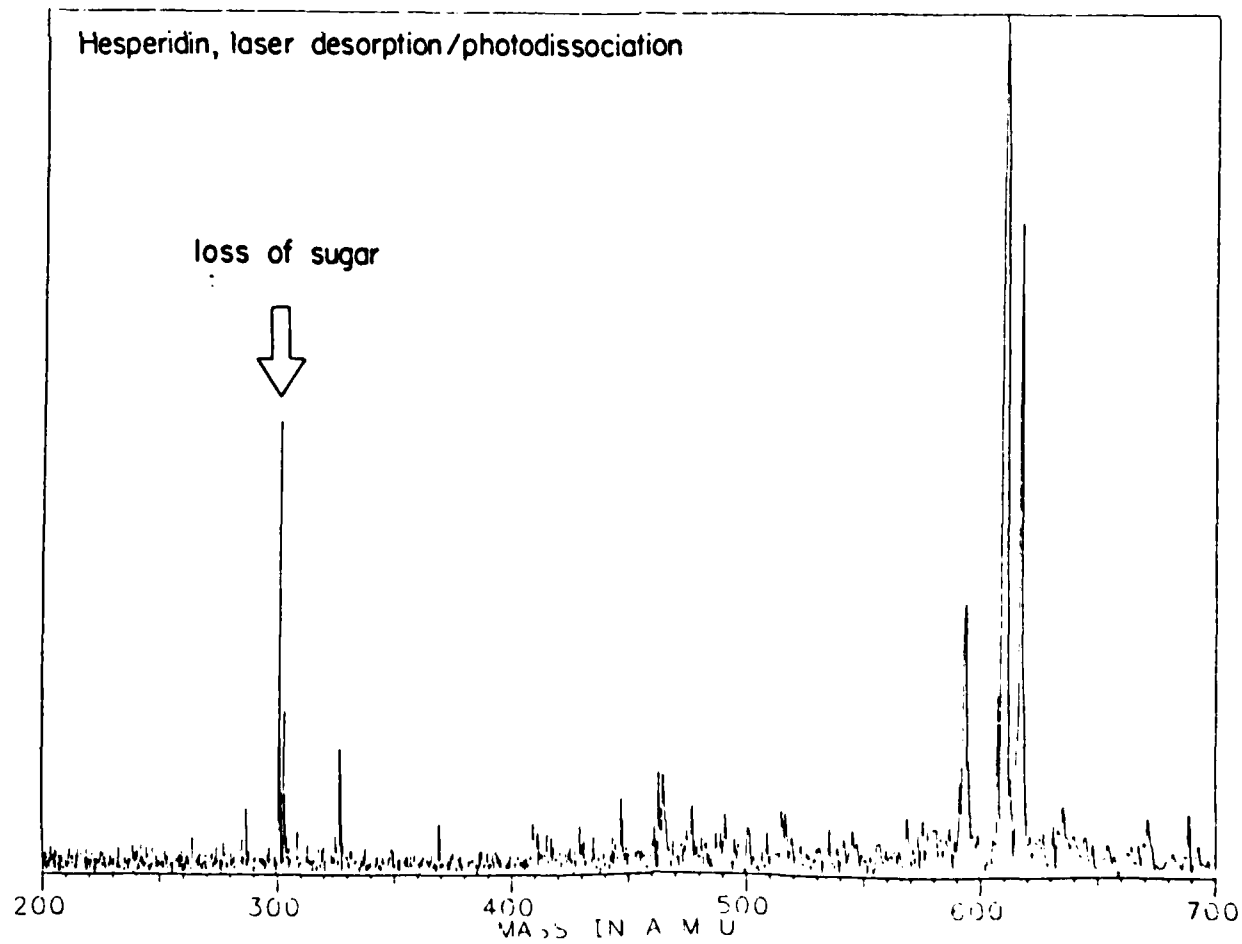
# Sucrose, laser desorption



Hesperidin, laser desorption

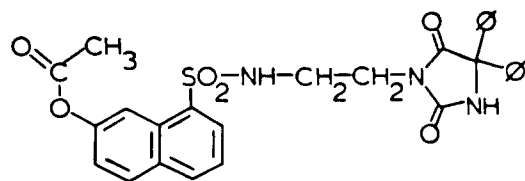


Hesperidin, laser desorption/photodissociation



Substituted sulfonamide, laser desorption

$(M - C_2H_3O)^-$



200 250 300 350 400 450 500 550 600

Substituted sulfonamide, laser desorption / photodissociation

$(M - C_2H_3O)^-$

$C_{15}H_{11}O_2N_2^-$

200 250 300 350 400 450 500 550 600  
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